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(U) Computer Modeling of Soot Formation Comparing Free Radical and Ionic Mechanisms

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A collaborative effort has been initiated between AeroChem and Penn State to compare the relative importance of the free radical mechanism of Frenklach and associates and the ionic mechanism of Calcote and associates by use of a computer program run at Penn State. During the present report period: the thermodynamic data for some neutral species and the ions employed in the ionic mechanism were either compiled from the literature or calculated; the reaction mechanism was developed and the rate coefficients either obtained from the literature or estimated; and the ambipolar diffusion coefficients of the ions involved were calculated. Considerably more work is yet required in estimating the reaction rate coefficients. Comparative computer runs will first be made on the well documented sooting acetylene/oxygen/argon flat flame at a pressure of 1.67 kPa and a linear flow rate of 50 cm/s.

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I. INTRODUCTION

This is the first annual report on this program which is a collaborative effort between AeroChem (Principal Investigator: H. F. Calcote) and Penn State (Principal Investigator: M. Frenklach. The ultimate objective is to develop a quantitative model of soot formation in flames that is consistent with experimental data. The specific objectives of this collaborative three-year study are: (1) to delineate the relative importance of the neutral free radical and ionic mechanisms of soot formation in flames; (2) to determine the optimum model of the total soot formation process based upon what is currently known; and (3) to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

In this report, the AeroChem effort is reviewed; the Penn State effort is covered in their companion report.[1] AeroChem is responsible for the development of the thermodynamics, diffusion coefficients, reaction mechanism, and reaction rate coefficients for the ionic mechanism. There were no previous sets of data on the ionic mechanism to draw upon when we initiated this program; two papers were subsequently published by Brown and Eraslan,[2,3] in which they calculated the concentrations of ions in both stoichiometric and fuel rich flames and compared the calculations with experiments. For the sooting flames we wished to model in this program, it has been necessary not only to construct the ionic mechanism and identify the rate coefficients but also to develop neutral mechanisms and to organize data for odd number neutral carbon compounds. Such species are not generally utilized in the free radical mechanisms of soot formation. Odd carbon neutral species play a significant role in the ionic mechanism and are observed in relatively large concentrations in sooting flames. There are some difficulties in defining the ionic mechanism for pyrolysis conditions because there is no known route to the CH^* without the presence of oxygen (CH^*, the first electronic state of CH ($A^2\Delta$) seems to be required to explain the formation of ions). Ions are observed in shock tube pyrolysis even when great effort is taken to remove oxygen.[4]

Preliminary computer experiments were carried out for a shock tube to obtain some feel of how the ionic mechanism performed in the computer program, and to work out some of the details of the mechanism. This is not a good system in which to compare the two mechanisms because there are no ion profile data. The first computer modeling results on a flame system are being compared with the well-documented acetylene/oxygen flame burning on a flat flame burner at a pressure of 1.67 kPa (20 Torr) and a linear flow rate of 50 cm/s in the unburned gases. In our previous AFOSR contract work,[4-6] we duplicated the burner Bittner and Howard[7] used to obtain neutral species concentrations and we measured ion concentration profiles with this burner so the ion profiles and the neutral profiles would be from the same system. We also compared the data obtained by a number of other researchers on very nearly the same flame; we previously presented the results of this comparison[5] which showed amazing agreement among several laboratories. This data base forms an excellent experimental standard with which to compare the computer modeling results.

II. STATEMENT OF WORK

A. Organize relevant data on ion-molecule reactions, thermochemistry, electron attachment, ion recombination, and ion and electron diffusion to be used in the computer code simulation by Penn State.

B. Determine the hydrogen atom concentration in the "well-studied" C_2H_2/O_2 flame and determine if this concentration exceeds the thermal equilibrium concentration.

C. Analyze the computer simulation data obtained by Penn State and compare the results with available experimental data to determine the major chemical pathways to incipient soot and to simplify the computer model.

D. Organize relevant data on the elementary steps involved in the growth of incipient soot to soot particles, including growth by molecular addition, coagulation, and oxidation.

E. Analyze the computer simulation data obtained by Penn State using the extended model and compare the results with available experimental data to determine the major pathways to particulate soot and to determine how to alter the model to make it more in conformity with experimental results.

F. Review the literature and choose flame experiments with which to compare the model developed above.

G. Analyze the computer simulation data obtained by Penn State and compare the results with the experimental data to determine the general applicability of the model and to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

III. THERMODYNAMICS

The required thermodynamic data for most of the ions and some of the neutral species were either collected from the literature or calculated. Available compilations of data for ions, e.g., Refs. 8-10 contain very few odd number carbon atom compounds; experimentally these species dominate in the flame mass spectra. The compilations also do not include isomers, which are of interest. Thermodynamic data for these species were generated as described below.

Data on a number of species, e.g., vinyl radical, C_3H_2 isomers, $C_2H_3^+$ isomers, $C_3H_3^+$ isomers, $C_7H_5^+$, $C_8H_7^+$, $C_{10}H_9^+$, and several larger ions, were recalculated, based upon new thermodynamic

information. We note that in the new edition of the JANNAF Tables[11] the heats of formation and free energies of formation for acetylene are incorrect; we use the data in the old tables (2nd Ed.). For example, at 2000 K the value in the new JANNAF and the old (correct) values are: for $\Delta H_f°$ 167 and 221 kJ/mol; and for $\Delta G_f°$ 441 and 118 kJ/mol.

The results are presented in Tables I and II, in which extensive footnotes explain the means of arriving at the data. The structures of the ions are given in Figs. 1 and 2.

The thermodynamic quantities, $C_p°$ and S° for hydrocarbons and hydrocarbon ions, were calculated, when sufficient information was available from vibrational frequencies and moments of inertia, using statistical mechanical methods, or following Benson's thermochemical methods of group additives. Enthalpies of formation at 298 K, $\Delta H_f°$ 298, were obtained either directly from the literature or calculated from experimental proton affinities and the corresponding neutral molecule's enthalpy of formation.

Unfortunately, there are several neutral molecules for which the thermodynamic data are uncertain. This is, for example, the case with diacetylene, an important reactant in the ionic mechanism. The available heats of formation at 298 K range from 439 to 473 kJ/mol.[12-16] We have used 440 kJ/mol[12] because the data in this reference were used previously in several thermochemical calculations with large ions. This uncertainty will be manifest in the flame simulations when rates for reverse chemical reactions are calculated from thermodynamics and forward reaction rate coefficients. For a few cases, such as for the cyclopropenyl ion, $C_3H_3^+$, another important participant in the ionic mechanism, there was sufficient experimental information to employ the more accurate statistical mechanical methods to calculate $C_p°$ and S°.

The additional thermodynamic work to be done includes extending the data base to include larger ions and additional isomers, and updating the data for individual species as new information becomes available.

IV. REACTION MECHANISM AND REACTION COEFFICIENTS

The overall mechanism is shown in Fig. 3. The ionic path starts when electronically excited CH (CH^*) reacts with an oxygen atom to produce HCO^+, which, through a series of ion-molecule reactions, produces $C_3H_3^+$, an ion which is observed in large concentrations in fuel rich and sooting flames. This ion then reacts with any of six small neutral species, indicated in Fig. 3, to produce larger ions which continue to grow through a series of ion-molecule reactions with the same six species[5] producing larger and larger ions. To simplify the number of reactions which have to be handled we have only considered C_2H_2, C_4H_2 and C_3H_4 in the reaction set. We should be able to eliminate some of the reactions in this set as not playing a major role. Simultaneously as the ions grow, they are neutralized at a rate which increases with increasing mass, producing "neutral

reactants," polycyclic aromatic hydrocarbons, that, of course, can continue to grow to soot through the "neutral mechanism." The ion-molecule reactions form a path to these large neutrals. These neutral reactions have not yet been incorporated into the mechanism at this stage of its development; they would be the same reactions included in the Frenklach et al. neutral mechanism.

The complete reaction mechanism with reaction rate coefficients, and heats of reaction and free energies of reaction at 2000 K, is presented in Table III as it presently exists. The mechanism in this form has not yet been evaluated in the computer model, and is far from being considered satisfactory. The AeroChem strategy has been to assemble a complete, but preliminary, ionic reaction model so that Frenklach and Wang[1] can exercise the computer program and work out any computer problems resulting from including ions in the mechanism while we continue to improve the model by further literature searches and improved numerical estimates.

Some of the major difficulties encountered in developing the ionic mechanism involve neutral species reactions and especially those which form electronically excited CH^* and C_2^*. CH^* and C_2^* are important in the production of the initial chemiions that drive the process. Their rates of formation are not well known.

In developing this mechanism only ionic species which have been observed in sooting flames have been included. There are several excellent sources of ion-molecule rate coefficients, including some for the reactions included in this mechanism. The measured reaction rate coefficients for ion-molecule reactions are generally consistent with Langevin theory. In addition, correlating principles have been developed to estimate the relative rates of ion-molecule reactions but these have not yet been applied to this set of reactions. Now that the thermodynamic data base has been developed, we will apply such principles to the data during the next year of this program. The temperature effect on the rate of ion-molecule reactions is not well understood although there are some theoretical considerations available which indicate a negative temperature coefficient. This will also be considered in future work.

We are working to reduce the number of reactions required to describe the ionic route to soot. The mechanism currently includes isomers of some large ions. Since ions generally isomerize very rapidly, the isomers can be considered to be in equilibrium. We will use this to reduce the number of reactions, taking into account the "reasonableness" of each reaction. Further, we have written all of the ion-molecule reactions to be exothermic in the forward direction to limit the maximum rate to a reasonable value. In some cases this leads to a smaller molecular product, i.e., the reaction is leading away from soot. The reverse reaction, i.e., toward ion growth, is then governed by ΔH_f° and ΔG_f°. The ΔH_f° and ΔG_f° values at 2000 K, see Table III, clearly demonstrate the important role of entropy at high flame temperatures. This will be taken into account in the future by using ΔS° in estimating the temperature coefficient, n, for reaction rate coefficients.

In choosing product channels for the large ion-electron dissociative recombination reactions, only molecules observed by Bockhorn et al.[17] have been considered as products. Reaction rate coefficients for ion-electron reactions are not strongly temperature dependent, but they do increase

with the size of the ion. This rate coefficient increase has not yet been incorporated into this data set. Clearly much work remains in developing the ionic mechanism.

V. DIFFUSION

Because the pressure for the standard flame is less than one atmosphere and we have experimentally demonstrated the importance of diffusion[5] in the flame chosen for study, it is necessary to include the diffusion coefficients for ions. We estimated these using the procedure previously developed for interpreting Langmuir probe data.[6] Experimental ion mobilities of a wide mass range of PCAH ions[18,19] were extrapolated to the higher mass range required for this program. This extrapolation gives results of μ vs. ionic mass, amu, which parallels the results obtained from a calculation using the Langevin type equation, giving confidence in the procedure.

We assume that the negative species is a free electron, although there is some evidence that there are large negative ions present.[4,20] With electrons present the ambipolar diffusion coefficient of the ion must be used because the ions do not diffuse independent of electrons. The ambipolar diffusion coefficient (D_a) for a specific ion was calculated from the ion mobility using the relationship[21]: $D_a = 2kT\mu/e$, where k is Boltzmann's constant, T is temperature, μ is the ion mobility, and e is the elementary charge, 1.602E-19 J. The ionic mobility is calculated by the following procedure:

(1) Calculate the ion mobility, μ, at 2.67 kPa and 273 K for each of the dominant flame gases using the following correlations developed at AeroChem based on the Langevin equation combined with experimental values:

$$\mu_{i,j}(P_0, T_0) = a(j) \times (MW_i)^{b(j)} \ cm^2 \ V^{-1} \ s^{-1}$$

where i is the ion species of mass MW_i and where a(j) and b(j), for each flame gas, j, are given in the following table: r^2 is the coefficient of determination of the fit to the actual data:

Gas	a	b	r^2
H_2	3471.53	-0.49893	0.9981
O_2	742.83	-0.48710	0.9981
CO_2	493.44	-0.46446	0.9975
C_2H_2	473.39	-0.43385	0.9991
CO	688.39	-0.47242	0.9989
H_2O	760.55	-0.46498	0.9984

(2) Correct each of the low pressure, low temperature ion mobilities calculated above, to flame pressures and temperatures, by the following formula (except for water), where P is the flame pressure (kPa) and T is temperature of the flame:

$$\mu_{i,j}\ (P,\ T) \quad = \quad \frac{P_0}{P} \times \left[\frac{T}{T_0}\right]^{0.72} \times \quad \mu_{i,j}\ (P_0,\ T_0)$$

For water vapor:

$$\mu_{i,H2O}\ (P,\ T) \quad = \quad \frac{P_0}{P} \times \left[\frac{T}{T_0}\right]^{1.16} \times \quad \mu_{i,H2O}\ (P_0,\ T_0)$$

(3) Correct the ion mobility calculated for each of the pure gases, and evaluated at flame conditions, to the actual flame gas composition using Blanc's Law - i.e., a simple viscosity mixing rule;

$$\mu_i^{-1}\ (\text{for the gas mixture}) = \sum_j \frac{X_j}{\mu_{i,j}}$$

where X_j is the mole fraction of gas j in the flame, and μ_i is the overall ion mobility of the ith ion in the gas mixture.

It was apparently difficult to incorporate this into the computer program at this time so that a different procedure was actually used.[1]

VI. PUBLICATIONS

There have been no publications on this program to date, but we list publications from a previous AFOSR program (Contract F49620-83-C-0150) which have not been reported; these set the background for the present work:

1. Calcote, H.F., Olson, D.B., and Keil, D.G., "Are Ions Important in Soot Formation?" Energy & Fuels 2, 494-504 (1988).

2. Calcote, H.F. and Keil, D.G., "Ion-Molecule Reactions in Sooting Acetylene-Oxygen Flames," Combust. Flame 74, 131-146 (1988).

VII. PROFESSIONAL PARTICIPATION

The Principal Investigator on the program is H. F. Calcote who has been responsible for developing the reaction mechanism and collecting the reaction kinetics data. Dr. R. J. Gill has been responsible for collecting and calculating the thermodynamics data. We both acknowledge fruitful discussions with Drs. W. Felder and D. G. Keil.

VIII. TECHNICAL INTERACTIONS

1. Poster on "An Ionic Mechanism of Carbon Formation in Flames" at NASA Symposium "Carbon in the Galaxy," Ames Laboratory, California, 5, 6 November 1987.

2. Presentation on "Soot Formation in Flames" at NASA Lewis on 22 September, 1988.

IX. INVENTIONS

None.

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TABLE I
HEAT OF FORMATION, ENTROPY AND HEAT CAPACITY
FOR NEUTRAL AND RADICAL SPECIES

(Units: ΔH_f° kJ/mole; S° and C_p° J/mole·deg)

Formula[a]	ΔH_f° 298	S° 298	C_p° at Temperature, K 298	400	500	600	700	800	900
CH* ($A\ ^2\Delta$)	873	183	29.1	29.1	29.2	29.5	29.8	30.3	30.8
C_2H	565	213	41.9	44.0	45.5	46.9	48.4	50.0	51.7
C_2H_2	228	201	44.1	50.5	54.9	58.3	61.2	63.8	66.1
C_2H_3	277	234	42.1	49.7	56.4	62.2	67.1	71.4	75.1
C_3H_2 (a)	473	237	44.6	54.3	62.5	69.0	74.2	78.5	82.0
C_3H_2 (b)	544	248	53.0	59.3	65.1	70.2	74.6	78.4	81.8
C_3H_2 (c)	527	243	50.9	59.5	66.0	71.3	75.6	79.3	82.5
C_3H_3	344	261	58.9	69.0	76.8	83.1	88.4	93.0	97.0
C_3H_4 (a)	192	244	59.1	72.0	82.9	92.0	99.7	106.2	112.0
C_3H_4 (b)	186	248	61.0	72.5	82.5	91.1	98.6	105.1	110.8
C_3H_4 (c)	276	243	53.2	68.0	80.5	90.7	99.0	106.0	112.0
C_4H_2	440	249	73.7	84.3	91.4	96.8	101.3	105.1	108.4
C_4H_6	110	279	80.1	101.5	119.0	133.1	144.8	154.6	162.9
$C_{10}H_8$	151	333	132.5	180.1	219.8	251.5	277.0	297.7	314.9

TABLE I (Continued)

Formula[a]	$C_p°$ at Temperature, K 1000	1200	1400	1600	1800	2000	2500	3000	Note
CH* ($A\ ^2\Delta$)	31.3	32.3	33.2	33.9	34.5	34.9	35.7	36.2	1
C_2H	53.4	56.9	60.1	62.8	64.9	66.4	68.4	69.0	2
C_2H_2	68.3	72.1	75.2	77.8	79.9	81.6	84.9	87.1	3
C_2H_3	78.5	84.1	88.5	91.9	94.5	96.6	100.3	102.5	4
C_3H_2 (a)	85.1	89.9	93.4	96.1	98.2	99.8	102.5	104.1	5
C_3H_2 (b)	84.7	89.4	93.0	95.8	98.0	99.8	103.5	106.7	6
C_3H_2 (c)	85.3	89.8	93.3	95.9	98.0	99.6	102.3	103.9	7
C_3H_3	100.6	106.6	111.4	115.1	118.0	120.3	124.3	126.7	8
C_3H_4 (a)	117.0	125.2	131.4	136.2	139.9	142.8	147.6	150.5	9
C_3H_4 (b)	115.9	124.2	130.6	135.5	139.3	142.2	147.3	150.3	10
C_3H_4 (c)	117.1	125.4	131.6	136.4	140.1	142.9	147.8	150.6	11
C_4H_2	111.4	116.3	120.1	123.1	125.4	127.3	130.4	132.3	12
C_4H_6	170.1	181.7	190.7	197.6	203.0	207.1	213.9	218.0	13
$C_{10}H_8$	329.2	351.5	367.8	379.9	389.1	396.1	407.9	414.9	14

Notes[b]

1 CH^* designates the CH molecule in its first electronic excited state. The $C_p°$ and $S°$ of CH^* were calculated using RRHO-SM formulas together with the data reported in Refs. 1, 2. $\Delta H_f°(CH^*) = \Delta H_f°$(CH, Ref. 1) + energy difference between ground and first electronic states (= 279 kJ/mol, Ref. 2).

2 The $\Delta H_f°$ of ethynl radical is from Refs. 3, 4. The $C_p°$ and $S°$ were estimated by RRHO-SM formulas together with the structure and vibrational frequencies listed in Refs. 5-8. The entropy is corrected for the first low lying electronic state of ethynl radical, which is about 4000 cm^{-1} above ground state.

3 The $\Delta H_f°$ of acetylene is from Ref. 9. The $C_p°$ and S° data are from Ref. 1, which were calculated from SM + ANH formulas. The $C_p°$ and S° values reported in Ref. 1 compared well with both the RRHO-SM estimated values which we calculated and the fitted experimental values of Ref. 10.

4 The $\Delta H_f°$ of vinyl radical is from Ref. 11. The $C_p°$ and S° values were calculated by RRHO-SM formulas with structure and vibrational frequencies reported in Refs. 12, 13.

5 The $\Delta H_f°$ of cyclopropylidene is from Ref. 14. $C_p°$ and S° values were estimated by RRHO-SM formulas. The vibrational frequencies and structure were calculated by QM methods in Ref. 15, but we multiplied the vibrational frequencies by 0.9 to give closer agreement to the experimental data listed in Ref. 5.

6 The $\Delta H_f°$ of vinylidene carbene is from Ref. 14. $C_p°$ and S° were estimated by RRHO-SM formulas. The QM calculated structure and vibrational frequencies are from Ref. 16. The vibrational frequencies were multiplied by 0.95 to give better agreement with experimental data listed in Ref. 16.

7 The $\Delta H_f°$ of the propargylene diradical is from Refs. 14 and 17. $C_p°$ and S° were calculated by RRHO-SM formulas together with the QM calculated structure of Ref. 14. Four of the nine vibrational frequencies for propargylene have not been experimentally identified and QM calculations have not been performed to predict the full set of vibrational frequencies. Therefore, as a compromise, vibrational frequencies calculated for the $^3A_2$ state of cyclopropenylidene, predicted to be a "broken" or "open" ring structure, were employed (Ref. 15). The QM calculated frequencies were multiplied by 0.9 to give better agreement with the few experimental vibrational frequencies listed in Ref. 16.

8 The $\Delta H_f°$ of 3-propynl radical is from Refs. 18 and 19. $C_p°$ and S° were calculated by RRHO-SM formulas using the structure and vibrational frequencies of Ref. 20. The vibrational frequencies of Ref. 20 were multiplied by 0.94 to fit the limited experimental data given in Ref. 5.

9 The $\Delta H_f°$ of allene is from Ref. 10. $C_p°$ and S° were estimated by RRHO-SM formulas using the structure reported in Ref. 21 and the vibrational frequencies of Ref. 22.

10 The $\Delta H_f°$ of propyne is from Ref. 10. $C_p°$ and S° were estimated by RRHO-SM formulas using the structure reported in Ref. 21 and the vibrational frequencies of Ref. 22.

11 The $\Delta H_f°$ of cyclopropene is from Ref. 23. $C_p°$ and S° were calculated by RRHO-SM formulas using structure from Ref. 24 and vibrational frequencies of Ref. 25.

12 The $\Delta H_f°$ of diacetylene is from Ref. 26. $C_p°$ and S° were estimated by RRHO-SM formulas with the molecular structure of Ref. 21 and vibrational frequencies of Ref. 22.

13 The $\Delta H_f°$ of butadiene is from Ref. 10. $C_p°$ and S° were calculated using GAB methods with group additivity values from Ref. 27 and 26.

14 The $\Delta H_f°$, structure and vibrational frequencies of naphthalene were taken from Ref. 28. The $C_p°$ and S° were calculated by RRHO-SM formulas.

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[a] Structures for molecules in Tables I and II are given in Figs. 1 and 2.

[b] Key to the abbreviations used in Notes sections for Tables I and II:

BDE	Abbreviation for bond dissociation energy. This is the minimum energy required to break a chemical bond forming two radicals. If the chemical bond is broken to yield an ion pair, the energy required is referred to as an "ionic BDE" in the Notes.
GAB	Abbreviation for the group additivity methods of Benson. These methods are fully described in Ref. 27.
IP	The ionization potential for a molecule is abbreviated as IP.
PA	The abbreviation for the proton affinity of a molecule.
PAH	Abbreviation for polycyclic aromatic hydrocarbon.
QM	Quantum mechanical calculations were performed to estimate one or all of the following properties: the electronic energy levels, structure and/or vibrational frequencies.
RRHO-SM	Rigid rotor harmonic oscillator statistical mechanics formulas were employed to calculate $C_p°$ and S°. The use and limitations of these formulas are described in standard physical chemistry textbooks (see Refs. 29 and 30).
SM + ANH	The rigid rotor harmonic oscillator statistical mechanics formulas are improved by the inclusion of spectroscopic anharmonic correction terms. These formulas are listed in the preface to the JANNAF tables (Ref. 1).

TABLE II

HEAT OF FORMATION, ENTROPY AND HEAT CAPACITY FOR CATIONS

(Units: ΔH_f° kJ/mole; S° and C_p° J/mole·deg)

Formula[a]	ΔH_f° 298	S° 298	C_p° at Temperature, K 298	400	500	600	700	800	900
CH_3^+	1093	187	34.8	37.8	41.4	45.1	48.6	51.9	54.9
$C_2H_3^+$ (a)	1113	226	49.9	56.9	62.7	67.7	72.1	75.9	79.4
$C_2H_3^+$ (b)	1119	224	47.2	54.7	60.9	66.1	70.7	74.7	78.2
$C_3H_3^+$ (a)	1073	231	49.4	63.3	74.9	84.0	91.1	96.9	101.5
$C_3H_3^+$ (b)	1178	251	60.3	70.0	78.2	84.3	89.6	94.3	98.7
$C_4H_3^+$	1217	276	70.9	83.7	93.9	101.5	108.1	113.9	118.9
$C_4H_5^+$ (a)	998	284	77.8	96.6	111.7	123.3	133.1	141.5	148.7
$C_4H_5^+$ (b)	1059	357	72.0	89.8	105.4	118.3	128.9	137.7	145.0
$C_5H_3^+$ (a)	1317	310	89.5	104.1	114.7	123.3	130.3	136.3	141.6
$C_5H_3^+$ (b)	1275	304	68.7	85.8	98.2	107.0	113.7	119.1	123.5
$C_5H_5^+$ (a)	1146	318	94.0	113.4	128.9	141.3	151.8	160.8	168.4
$C_5H_5^+$ (b)	1012	307	89.8	110.5	128.3	142.3	154.0	163.7	171.9
$C_6H_5^+$ (a)	1176	340	108.8	129.3	145.3	158.6	169.8	179.4	187.9
$C_6H_5^+$ (b)	1139	283	79.5	106.5	130.2	148.4	163.4	175.8	186.2
$C_7H_5^+$ (a)	1392	368	123.5	147.4	165.7	180.1	192.2	202.5	211.3
$C_7H_5^+$ (b)	1364	342	123.0	148.3	168.5	184.0	196.7	207.3	216.2
$C_7H_7^+$ (a)	898	330	104.7	137.4	165.6	188.5	207.2	222.6	235.5
$C_7H_7^+$ (b)	849	315	95.9	131.7	161.7	185.9	205.4	221.4	234.7
$C_8H_7^+$	998	344	120.6	155.0	184.9	208.1	227.4	243.7	257.3
$C_9H_7^+$ (a)	1144	363	132.4	171.6	203.4	228.8	248.9	265.4	279.1
$C_9H_7^+$ (b)	1007	336	127.0	161.8	196.0	222.9	245.0	263.5	279.0
$C_{10}H_9^+$ (a)	865	363	158.4	204.5	242.1	273.1	298.0	318.1	334.6
$C_{10}H_9^+$ (b)	1051	403	150.9	195.4	232.7	262.8	287.4	307.7	324.9
$C_{11}H_9^+$ (a)	1074	385	157.2	205.8	246.8	280.3	307.5	329.9	348.4
$C_{11}H_9^+$ (b)	1146	431	165.2	213.6	253.0	284.4	309.9	330.8	348.3
$C_{12}H_9^+$ (a)	933	368	148.9	204.8	250.4	289.0	320.4	345.7	366.3

TABLE II (Continued)

Formula[a]	C_p° at Temperature, K 1000	1200	1400	1600	1800	2000	2500	3000	Notes
CH_3^+	57.7	62.4	66.2	69.1	71.4	73.3	76.4	78.3	1
$C_2H_3^+$ (a)	82.4	87.5	91.4	94.4	96.7	98.5	101.6	103.4	2
$C_2H_3^+$ (b)	81.3	86.6	90.6	93.7	96.1	98.0	101.2	103.2	3
$C_3H_3^+$ (a)	105.4	111.4	115.7	119.0	121.4	123.3	126.5	128.3	4
$C_3H_3^+$ (b)	102.8	110.2	116.4	121.8	126.4	130.3	138.2	144.0	5
$C_4H_3^+$	123.2	130.2	135.4	139.3	142.4	144.8	149.0	151.6	6
$C_4H_5^+$ (a)	154.9	164.7	172.1	177.6	181.9	185.3	191.3	195.1	7
$C_4H_5^+$ (b)	151.3	161.1	168.5	174.2	178.8	182.5	189.3	193.9	8
$C_5H_3^+$ (a)	146.4	155.0	162.5	169.0	174.8	179.8	190.2	198.1	9
$C_5H_3^+$ (b)	127.2	132.9	137.0	140.1	142.5	144.4	147.7	149.8	10
$C_5H_5^+$ (a)	175.0	185.7	193.9	200.3	205.3	209.5	217.1	222.2	11
$C_5H_5^+$ (b)	178.7	189.3	197.0	202.8	207.2	210.6	216.5	220.1	12
$C_6H_5^+$ (a)	195.5	208.5	219.3	228.5	236.3	243.0	256.5	266.4	13
$C_6H_5^+$ (b)	194.9	208.4	218.2	225.4	230.9	235.2	242.4	246.9	14
$C_7H_5^+$ (a)	218.9	230.9	240.1	247.2	252.8	257.4	265.6	271.1	15
$C_7H_5^+$ (b)	223.6	235.3	243.7	250.0	254.8	258.6	265.1	269.1	16
$C_7H_7^+$ (a)	246.4	263.6	276.5	286.2	293.6	299.1	307.4	311.0	17
$C_7H_7^+$ (b)	245.9	263.6	276.7	286.6	294.1	299.9	309.3	315.0	18
$C_8H_7^+$	268.8	286.8	299.9	309.6	317.0	322.8	332.6	338.7	19
$C_9H_7^+$ (a)	290.8	309.9	324.8	337.0	347.1	355.6	372.0	383.8	20
$C_9H_7^+$ (b)	291.9	311.9	326.2	336.7	344.6	350.7	360.9	367.0	21
$C_{10}H_9^+$ (a)	348.1	369.0	384.3	396.0	405.0	412.3	425.5	434.3	22
$C_{10}H_9^+$ (b)	339.6	363.8	383.0	398.6	411.6	422.5	443.0	456.1	23
$C_{11}H_9^+$ (a)	363.9	388.3	406.5	420.5	431.7	440.7	457.2	468.3	24
$C_{11}H_9^+$ (b)	363.0	386.5	403.9	417.0	426.8	434.1	444.5	448.5	25
$C_{12}H_9^+$ (a)	383.1	408.8	427.2	441.0	451.6	460.0	474.8	484.5	26

TABLE II (Continued)

Formula[a]	$\Delta H_f°$ 298	S° 298	$C_p°$ at Temperature, K 298	400	500	600	700	800	900
$C_{12}H_9^+$ (b)	1160	405	173.2	223.4	266.2	299.8	327.6	350.8	370.3
$C_{12}H_9^+$ (c)	1160	405	173.5	223.8	266.7	300.3	328.0	351.2	370.6
$C_{13}H_9^+$	1115	352	144.9	197.5	242.3	276.6	304.4	327.4	346.5
$C_{14}H_{11}^+$	1117	411	167.5	224.7	273.4	312.9	345.0	371.3	393.1
$C_{15}H_{11}^+$	1180	434	210.2	275.5	330.6	373.6	409.0	438.3	462.7
$C_{16}H_{11}^+$ (a)	883	470	224.9	299.2	357.7	403.4	439.7	468.9	492.7
$C_{16}H_{11}^+$ (b)	1301	450	219.0	288.4	344.8	390.6	427.4	457.3	482.0
$C_{17}H_{11}^+$ (a)	1140	449	226.3	300.2	360.6	409.1	447.9	479.3	505.0
$C_{17}H_{11}^+$ (b)	982	433	222.5	296.6	358.6	406.8	446.2	478.6	505.4
$C_{18}H_{11}^+$ (a)	1238	452	237.4	311.6	374.2	423.4	463.9	497.3	525.0
$C_{18}H_{11}^+$ (b)	1109	469	244.8	322.7	387.6	438.0	479.1	513.0	541.0
$C_{18}H_{11}^+$ (c)	1008	423	220.1	300.8	365.6	418.6	461.2	495.4	523.1
$C_{19}H_{11}^+$	986	431	239.1	322.6	391.2	443.9	486.3	520.8	549.0
$C_{20}H_{11}^+$ (a)	1234	458	253.3	338.6	405.8	460.2	503.9	539.0	567.5
$C_{20}H_{11}^+$ (b)	1080	473	253.9	337.6	406.8	460.5	504.0	539.4	568.7
$C_{21}H_{11}^+$	1129	474	263.1	352.6	425.5	481.4	526.1	562.4	592.1
$C_{22}H_{13}^+$	957	558	289.6	386.8	464.9	526.0	574.4	613.2	644.6
$C_{23}H_{13}^+$	1066	503	291.7	391.0	472.5	535.6	586.4	627.9	662.0
$C_{24}H_{13}^+$	993	557	306.2	412.8	497.5	563.0	614.5	655.4	688.3

TABLE II (Continued)

Formula[a]	C_p° at Temperature, K 1000	1200	1400	1600	1800	2000	2500	3000	Notes
$C_{12}H_9^+$ (b)	386.5	411.8	430.0	443.4	453.7	461.6	475.0	483.1	27
$C_{12}H_9^+$ (c)	386.9	412.0	430.2	443.6	453.8	461.7	475.1	483.2	28
$C_{13}H_9^+$	362.5	387.1	404.9	418.1	428.1	435.8	449.0	457.1	29
$C_{14}H_{11}^+$	411.4	440.1	461.7	478.3	491.6	502.3	522.1	535.4	30
$C_{15}H_{11}^+$	483.1	514.6	537.3	554.0	566.7	576.5	593.1	603.2	31
$C_{16}H_{11}^+$ (a)	512.3	542.5	564.3	580.7	593.3	603.4	621.2	632.8	32
$C_{16}H_{11}^+$ (b)	503.0	536.6	562.5	583.1	600.0	614.1	641.0	660.0	33
$C_{17}H_{11}^+$ (a)	526.3	559.4	583.7	602.2	616.8	628.5	649.7	663.8	34
$C_{17}H_{11}^+$ (b)	527.6	561.7	586.1	604.0	617.5	627.9	645.4	656.0	35
$C_{18}H_{11}^+$ (a)	548.0	583.3	608.5	627.0	640.9	651.5	669.5	680.3	36
$C_{18}H_{11}^+$ (b)	564.3	600.2	625.9	644.8	659.0	670.1	688.7	700.1	37
$C_{18}H_{11}^+$ (c)	545.8	580.0	604.5	622.5	636.2	647.0	665.8	677.7	38
$C_{19}H_{11}^+$	572.3	607.9	633.2	651.7	665.6	676.3	694.3	705.2	39
$C_{20}H_{11}^+$ (a)	590.8	626.0	651.1	669.6	683.7	694.7	713.7	725.7	40
$C_{20}H_{11}^+$ (b)	592.8	629.5	655.6	674.7	689.0	700.0	718.4	729.5	41
$C_{21}H_{11}^+$	616.5	653.6	679.9	699.1	713.5	724.6	743.2	754.4	42
$C_{22}H_{13}^+$	670.1	708.7	736.0	755.8	770.8	782.4	802.1	814.2	43
$C_{23}H_{13}^+$	690.1	732.9	763.3	785.5	802.2	815.1	836.7	849.7	44
$C_{24}H_{13}^+$	715.0	755.0	783.1	803.5	818.8	830.5	850.4	862.5	45

Notes[b]

1 The ΔH_f° of the methyl cation is from Refs. 9 and 31. The heat capacity and entropy were calculated by RRHO-SM formulas using structure and vibrational frequency data in Refs. 5, 32, 33.

2 The $\Delta H_f°$ for the cyclic or "non-classical" $C_2H_3^+$ cation is from Refs. 9 and 34. $C_p°$ and S° were calculated by RRHO-SM formulas with the structure and vibrational frequencies from Refs. 32 and 35.

3 The $\Delta H_f°$ for the vinyl cation is calculated using the data in Refs. 9, 34, and 35. $C_p°$ and S° were calculated by RRHO-SM formulas using the structure and vibrational frequencies from Refs. 32 and 35.

4 The $\Delta H_f°$ for cyclopropenyl cation is the average of data in Refs. 9 and 31. The heat capacity and entropy were calculated by RRHO-SM formulas with the structure from Ref. 36 and the vibrational frequencies of Ref. 37.

5 The $\Delta H_f°$ of propargyl cation is an average of data in Refs. 9 and 31. $C_p°$ and S° were calculated using Benson's group additivity methods (Refs. 26, 27) - these properties were calculated for a propyne parent molecule and then corrected for the loss of methyl C-H bond vibrations.

6 The $\Delta H_f°$ of the 2-but-1-yne-3-enyl cation is from Ref. 9. $C_p°$ and S° were calculated for vinylacetylene and then corrected for the loss of a C-H bond, using GAB methods (Refs. 26, 27).

7 The $\Delta H_f°$ 2-butadienyl cation is from Ref. 31. Heat capacity and entropy were calculated for butadiene, and then corrected for the loss of a C-H bond on an internal carbon atom using GAB methods (Refs. 26, 27).

8 The $\Delta H_f°$ of methyl-cyclopropenyl cation ($C_4H_5^+$) was estimated by the scheme: -BDE for a methyl group C-H bond of toluene (Ref. 38) = $\Delta H_f°(C_4H_5^+)$ - { $\Delta H_f°$(H atom, Ref. 1) + $\Delta H_f°$ (methylene-cyclopropenyl cation, Ref. 9)}. $C_p°$ and S° were estimated by adjusting the $C_p°$ and S° values of cyclopropenyl ion $C_3H_3^+$ (a) for the substitution of a C-H group (treated as an aromatic C-H bond) with a methyl group - using GAB methods (Refs. 26 and 27).

9 The $\Delta H_f°$ of the linear $C_5H_3^+$ cation (5-penta-1,3-diynyl cation) is from Ref. 31. $C_p°$ and S° were calculated using the group additivity values from Refs. 26 and 27.

10 The $\Delta H_f°$ for cyclic $C_5H_3^+$ cation (ethynyl-cyclopropenyl cation) was calculated from the $\Delta H_f°$ (cyclopropenyl cation, $C_3H_3^+$ (a)) and thermochemical group corrections (Refs. 26, 27). For comparison, the $\Delta H_f°$ is reported as 1280 kJ/mol·deg in Ref. 39. $C_p°$ and S° were calculated by replacing a C-H group of cyclopropenyl cation with an ethynl group, following Benson's group additivity methods (Refs. 26, 27).

11 The $\Delta H_f°$ for linear $C_5H_5^+$ cation (5-penta-1-yne-3-enyl cation) is an average of values reported in Refs. 9 and 31. The $C_p°$ and S° were calculated by group additivity data from Refs. 26 and 27, with thermochemical corrections for loss of a methyl hydrogen.

12 The $\Delta H_f°$ for vinyl-cyclopropenyl cation is from Ref. 9. $C_p°$ and S° were calculated by employing group additivity values from Ref. 26 to adjust the heat capacity and entropy for cyclopropenyl cation, $C_3H_3^+$ (a), following GAB methods (Ref. 27) .

13 $\Delta H_f°$ for linear $C_6H_5^+$ (5-hexa-1,3-diynyl cation) is from Ref. 31. $C_p°$ and S° were calculated from group additivities in Ref. 27 with thermochemical corrections for the loss of a C-H bond on the internal $-CH_2-$ group (i.e., vibrations and symmetry).

14 The $\Delta H_f°$ of the phenyl cation is from Refs. 9 and 31. The heat capacity and entropy were calculated from group additivities in Ref. 26, with thermochemical corrections for the loss of an aromatic C-H bond (vibrational modes and symmetry).

15 The $\Delta H_f°$ of 7-hepta-1,3-diynl-5-enyl cation ($C_7H_5^+$ (a)) was calculated by setting the ionic BDE of an allylic C-H bond = $\Delta H_f°(H^-$, Ref. 1) + $\Delta H_f°(C_7H_5^+)$ - $\Delta H_f°$ (hepta-1,3-diyne-4-ene, C_7H_6). The ionic BDE of an allylic C-H bond to yield the carbocation and H^-, was estimated in Ref. 40 as 1071 kJ/mol. Group additivity estimates for the $\Delta H_f°(C_7H_6)$ and for the heat capacity and entropy of the cation, were made using data from Refs. 26 and 27.

16 The $\Delta H_f°$ of $C_7H_5^+$ (1-ethynyl-2-vinyl-cyclopropenyl cation) was estimated from the $\Delta H_f°$(cyclopropenyl cation, $C_3H_3^+$ (a)), and the enthalpy contributions by vinyl and ethynl (C_2H) groups, using group values from Ref. 26. The heat capacity and entropy were calculated by the GAB method (Refs. 26, 27).

17 The $\Delta H_f°$ of benzyl cation is an average of data in Refs. 9 and 41. The $C_p°$ and S° were estimated by group additivity values given in Refs. 26 and 27.

18 The $\Delta H_f°$ for tropylium cation is from Ref. 9. Treating the tropylium ion as an aromatic molecule, the heat capacity and entropy were estimated using the group additivities for benzene C-H bonds (Ref. 26).

19 The $\Delta H_f°$ of styrenyl cation was found by solving: -(proton affinity of styrene, Ref. 42) = $\Delta H_f°(C_8H_7^+)$ - $\Delta H_f°(H^+$, Ref. 1) - $\Delta H_f°$ (phenylacetylene). The $\Delta H_f°$ of phenylacetylene was estimated by GAB methods (Ref. 26, 27). The $C_p°$ and S° were also calculated by GAB methods.

20 The $\Delta H_f°$ of 1-methylenyl-2-phenyl-acetylene cation ($C_9H_7^+$ (a)) was estimated by setting the ionic BDE of a propargyl C-H bond (= 1021 kJ/mol, Ref. 40) = $\Delta H_f°(H^-$, Ref. 1) + $\Delta H_f°$ ($C_9H_7^+$(a)) - $\Delta H_f°$ (C_9H_8, 1-phenylpropyne). The $\Delta H_f°$ of C_9H_8 is reported in Ref. 9. Group additivity for $C_p°$ and S° were estimated (Refs. 26, 27).

21 The $\Delta H_f°$ of the indenyl cation is from Ref. 43. Both the heat capacity and entropy were calculated by Benson's group additivity method using group data from Ref. 26 and 44.

22 The $\Delta H_f°$ for protonated naphthalene cation ($C_{10}H_9^+$ (a)) is from Ref. 9. The heat capacity and entropy were estimated by calculating the $C_p°$ and S° values for dihydronaphthalene using group additivity data in Refs. 26 and 27, and then corrected for the loss of a methylene C-H group in the cyclohexadiene ring (loss of 3 vibrational frequencies - 3000, 1400 and 700 cm^{-1}).

23 The $\Delta H_f°$ of 1-phenyl-3-butynyl cation ($C_{10}H_9^+$ (b)) was estimated by the calculation: -(proton affinity of styrene, Ref. 42) = $\Delta H_f°(C_{10}H_9^+$ (b)) - $\Delta H_f°(H^+$, Ref. 1) - $\Delta H_f°$ (1-phenyl-buta-1-yne-3-ene). The $\Delta H_f°$ of 1-phenyl-buta-1-yne-3-ene was calculated by Benson's group additivity method using data from Refs. 26 and 27. $C_p°$ and S° were also calculated by group additivity methods.

24 $\Delta H_f°$ for 2-methylenyl-naphthalene cation ($C_{11}H_9^+$ (a)) is an average of data in Refs. 9, 45 and 46. $C_p°$ and S° were calculated from group additivity corrections to a naphthalene parent molecule using data from Ref. 26 and 27.

25 The $\Delta H_f°$ for 1-phenyl-5-penta-1-yne-3-enyl cation ($C_{11}H_9^+$ (b)) was estimated from: -(proton affinity of allene, Ref. 47) = $\Delta H_f°(C_{11}H_9^+$ (b)) + $\Delta H_f°(H^-$, Ref. 1) - $\Delta H_f°$ ($C_{11}H_{10}$, 1-phenyl-5-penta-1-yne-3-ene). The $\Delta H_f°$ of $C_{11}H_{10}$ was calculated by group additivity data in Refs. 26 and 27. $C_p°$ and S° for $C_{11}H_9^+$ were also estimated by Benson's group additivity method.

26 The $\Delta H_f°$ of protonated acenaphthylene ($C_{12}H_9^+$ (a)) was approximated by: -(proton affinity of acenaphthane, Ref. 48) = $\Delta H_f°(C_{12}H_9^+$ (a)) - $\Delta H_f°$ (H^+, Ref. 1) - $\Delta H_f°$ (acenaphthylene). The $\Delta H_f°$ of acenaphthylene is reported in Ref. 49. The $C_p°$ and S° of $C_{12}H_9^+$ (a) were calculated from group additivity data in Refs. 26 and 27.

27 The $\Delta H_f°$ of 2-ethenyl-naphthalene cation, $C_{12}H_9^+$ (b), was estimated by: -(proton affinity of diacetylene, Ref. 50) = $\Delta H_f°(C_{12}H_9^+$ (b)) - $\Delta H_f°(H^+$, Ref. 1) - $\Delta H_f°$ (naphthyl-acetylene). The $\Delta H_f°$ of naphthyl-acetylene and the heat capacity and entropy of $C_{12}H_9^+$ (b) were estimated by group additivity corrections to a naphthalene parent molecule (Refs. 26, 27).

28 The $\Delta H_f°$ of 1-ethenyl-naphthalene cation ($C_{12}H_9^+$ (c)) was calculated using the scheme: -(proton affinity of diacetylene, Ref. 50) = $\Delta H_f°(C_{12}H_9^+$ (c)) - $\Delta H_f°$ (H^+, Ref. 1) - $\Delta H_f°$(naphthyl-acetylene). The $\Delta H_f°$ of naphthyl-acetylene, as well as the $C_p°$ and S° of $C_{12}H_9^+$ (c), were estimated by GAB methods and the data in Refs. 26 and 27.

29 The $\Delta H_f°$ of the phenalenyl cation ($C_{13}H_9^+$) was approximated by employing the scheme: ionization potential (IP) of 1H-phenalene = $\Delta H_f°(C_{13}H_9^+) + \Delta H_f°$ (H atom, Ref. 1) - $\Delta H_f°$ (1H-phenalene, Ref. 51). Both indene and 1H-phenalene are nonaromatic benzenoid ring systems and therefore should display similar ionization behavior. Thus, comparing the IP's for the two processes, indene + e^- = $(C_9H_7^+)$ + H + $2e^-$ (IP = 12.5 eV) with indenyl radical + e^- = $(C_9H_7^+)$ + $2e^-$ (IP = 8.4 eV), we find a difference of about 4.0 eV between the two types of ionization processes. The indene IP's are from experimental data reported in Refs. 45 and 46. The IP for simple ionization of 1H-phenalene (i.e., no loss of H), is calculated in Ref. 51 by QM calculations. This theoretical IP was corrected by substracting 0.5 eV, as this brings the theoretical and observed IP's for PAH's in closer agreement (see Preface of Ref. 51). Finally, 4.0 eV was added to this corrected simple IP to account for the H atom loss. The heat capacity and entropy were crudely estimated by GAB methods using data in Refs. 26 and 27, treating the cation as an aromatic molecule (i.e., all C-H bonds were treated as aromatic C-H bonds).

30 The $\Delta H_f°$ for methyl-phenalenyl cation was estimated using Benson's group additivity method (Ref. 27) by replacing an aromatic C-H group of the phenalene ($C_{13}H_9^+$) cation with a methyl group. The $C_p°$ and S° were estimated by GAB methods, in a similar fashion.

31 The $\Delta H_f°$ of vinyl-phenalenyl ($C_{15}H_{11}^+$) cation was estimated using Benson's group additivity method (Ref. 27) by replacing an aromatic C-H group of the phenalene ($C_{13}H_9^+$) cation with a vinyl group. The $C_p°$ and S° were estimated by the GAB method in a similar way.

32 The $\Delta H_f°$ of protonated pyrene ($C_{16}H_{11}^+$ (a)) was estimated from solving: -(proton affinity pyrene, Ref. 48) = $\Delta H_f°(C_{16}H_{11}^+$(a)) - $\Delta H_f°$(H^+, Ref. 1) - $\Delta H_f°$(pyrene). The $\Delta H_f°$ of pyrene is an average of a calculated group additivity value (Refs. 26, 27) and the reported values in Refs. 9, 49-52. The heat capacity and entropy were estimated by GAB methods (Refs. 26, 27).

33 The $\Delta H_f°$ of 1-propynl-phenalenyl cation ($C_{16}H_{11}^+$ (b)) was estimated thermochemically by removing an aromatic C-H bond of the phenalene cation ($C_{13}H_9^+$) and adding a propynl group contribution to the enthalpy. The $C_p°$ and S° were also estimated by group additivity methods using group data in Refs. 26 and 27.

34 The $\Delta H_f°$ of 2-methylenyl-pyrene cation ($C_{17}H_{11}^+$ (a)) was estimated by solving: Ionization potential (IP) of 2-methyl-pyrene = $\Delta H_f°$ (2-methylenyl-pyrene cation) + $\Delta H_f°$(H atom, Ref. 1) - $\Delta H_f°$(2-methyl-pyrene). The IP was estimated by noting that for methyl substituted aromatic hydrocarbons (i.e., 1 & 2-methyl-naphthalenes, 9-methyl-anthracene, and methyl-phenanthrenes), the IP accompanied by H atom loss, was higher by about 4.8 eV, than simple ionization (i.e., no H loss). This is based on experimental data reported in Ref. 49. Therefore, 4.8 eV was added to the simple IP (i.e., no H loss) calculated by QM methods in Ref. 51. As noted in the preface of Ref. 51, the theoretical IP's are about 0.5 eV higher than experimental IP data and therefore the theoretical IP was corrected for this as well. $C_p°$ and S° were calculated using Benson's methods (Refs. 26, 27).

35 The $\Delta H_f°$ of benz[d,e]anthracenyl cation ($C_{17}H_{11}^+$ (b)) from Ref. 43. $C_p°$ and S° were calculated using Benson's methods (Refs. 26, 27).

36 The $\Delta H_f°$ of benz[a]anthracenyl cation ($C_{18}H_{11}^+$ (a)) was calculated from: BDE of a benzene C-H bond (Ref. 38) = $\Delta H_f°(C_{18}H_{11}^+$ (a)) + $\Delta H_f°$(H atom, Ref. 1) - $\Delta H_f°(C_{18}H_{12}^+)$. The $\Delta H_f°(C_{18}H_{12}^+$, benz[a]anthracene ion) was calculated from setting IP(ave) = 720 kJ/mol = $\Delta H_f°(C_{18}H_{12}^+)$ - $\Delta H_f°(C_{18}H_{12})$, where the $\Delta H_f°$ of benz[a]anthracene ($C_{18}H_{12}$) is from Ref. 52. IP(ave) is the average of six reported IP values in Ref. 46. The heat capacity and entropy were calculated using Benson's methods (Refs. 26, 27 and 44).

37 The $\Delta H_f°$ of 2-vinyl-pyrene cation, $C_{18}H_{11}^+$ (b), was estimated from: -(proton affinity of pyrene, Ref. 48) = $\Delta H_f°(C_{18}H_{11}^+$ (b)) - $\Delta H_f°(H^+$, Ref. 1) - $\Delta H_f°(C_{18}H_{10})$. The $\Delta H_f°$ for $C_{18}H_{10}$, 2-ethynyl-pyrene, was found by Benson's group additivity methods (Ref. 27), together with the averaged $\Delta H_f°$ of pyrene (see Note 32). The heat capacity and entropy were calculated using Benson's methods (Refs. 26, 27).

38 The $\Delta H_f°$ of cyclopentyl-[c,d]-pyrene cation ($C_{18}H_{11}^+$ (c)) was estimated by the scheme: -(proton affinity of pyrene, Ref. 48) = $\Delta H_f°(C_{18}H_{11}^+$(c)) - $\Delta H_f°(H^+$, Ref. 1) - $\Delta H_f°(C_{18}H_{10})$. The $\Delta H_f°$ for $C_{18}H_{10}$ (cyclopenta-[c,d]-pyrene), was found by group additivity methods (Refs. 26, 27) together with the averaged $\Delta H_f°$ of pyrene (see Note 32). The $C_p°$ and S° were calculated using Benson's methods (Refs. 26, 27).

39 The $\Delta H_f°$ of benzo-[c,d]-pyrenyl cation ($C_{19}H_{11}^+$) is from Ref. 43. The heat capacity and entropy were calculated using Benson's methods (Refs. 26, 27).

40 The $\Delta H_f°$ of 1-ethynl-cyclopentyl-[c,d]-pyrene cation ($C_{20}H_{11}^+$ (a)) was obtained from enthalpy group additivities (Ref. 26, 27 and 44) by substitution of an ethynl group ($-C_2H$) in the $C_{18}H_{11}^+$ (c) ion above, for an aromatic C-H bond. The heat capacity and entropy were also calculated using GAB methods (Ref. 27).

41 The $\Delta H_f°$ for benzo-[e]-pyrenyl (BEP) cation ($C_{20}H_{11}^+$ (b)) was estimated using two thermodynamic schemes. For Scheme I we evaluated: BEP $\rightarrow$ (BEP^+) + e^- $\rightarrow$ ($BEPmh^+$) + H + e^-. BEPmh is the BEP parent molecule minus a hydrogen atom. The first step requires the ionization potential (IP) for BEP (= 7.43 eV = 717 kJ/mol, Ref. 46), which was set equal to the heat of reaction, H_{RXN}. In the second step, the heat of reaction was set equal to the negative value of an aromatic C-H bond dissociation energy, using an average of BDE's for five-membered ring aromatic C-H bonds calculated in Ref. 43. This average BDE was about 330 kJ/mol. So, for Scheme I, the $\Delta H_f°$ of $C_{20}H_{11}^+$ (b) is about 1110 kJ/mol. The second scheme (Scheme II) employed the definition of hydrogen atom affinity, HA (Eq. (12) of Ref. 48). The definition, when applied to this case is: HA = $-H_{RXN}$ = PA (BEPmh) + IP (BEPmh) - IP (H atom). If it is assumed that the PA for BEPmh is similar to pyrene (208.5 kJ/mol, Ref. 42) and the IP for BEPmh is similar to BEP, then we obtain another estimate for the H_{RXN} of the second step of Scheme I (= 277 kJ/mol). Thus, from the second scheme, $\Delta H_f°$ (BEP^+) is about 1050 kJ/mol. The average of these two estimated values was used for the $\Delta H_f°$ of BEP^+. This average value is close to similar sized PAH's listed in Ref. 43, where mostly odd carbon number PAH's were reported. The heat capacity and entropy were also calculated using GAB methods (Refs. 26, 27).

42 The $\Delta H_f°$ of cyclopentenyl-[e,d']-benzo-[c,d]-pyrene cation ($C_{21}H_{11}^+$) is from Ref. 43. $C_p°$ and S° were estimated using Benson's group additivity methods (Refs. 26, 27).

43 The $\Delta H_f°$ of protonated 1,12-benzoperylene cation ($C_{22}H_{13}^+$) from calculation: -(proton affinity of BP, Ref. 48) = $\Delta H_f°$ ($C_{22}H_{13}^+$) - $\Delta H_f°$ (BP) - $\Delta H_f°$ (H^+, Ref. 1), where BP is 1,12-benzoperylene (alternate name: benzo-[g,h,i]-perylene). The $\Delta H_f°$ of BP, and the $C_p°$ and S° of $C_{22}H_{13}^+$, were calculated using Benson's group additivity methods (Refs. 26, 27).

44 The $\Delta H_f°$ of the dibenzo-[a:c,d]-pyrene cation ($C_{23}H_{13}^+$) is from Ref. 43. The heat capacity and entropy were calculated by group additivities, as usual (Ref. 26, 27).

45 The $\Delta H_f°$ of protonated coronene ($C_{24}H_{13}^+$) is by calculation: - proton affinity of coronene (Ref. 48) = $\Delta H_f°$ ($C_{24}H_{13}^+$) - $\Delta H_f°$ (COR) - $\Delta H_f°$ (H^+, Ref. 1), where COR is coronene. The $\Delta H_f°$ (COR), and the $C_p°$ and S° of the cation, were calculated by group additivity methods (Refs. 26, 27).

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TABLE III
REACTION MECHANISM

Code for Molecular Structure: $C_3H_3^+ = C_3H_3^+(l)$; $H_3C_3^+ = C_3H_3^+(c)$; $C_3H_4 = C_3H_4$ (allene); $H_4C_3 = C_3H_4$ (propyne); $C_6H_5^+ = C_6H_5^+$ (l); $C_7H_7^+$ = benzyl; C_3H_2 = H-C•=C=C•-H; HC = CH^* (electronic state: A $^2\Delta$); $C_xH_y^+$, $H_yC_x^+$, and C_xH_y-1H represent three different isomers of the same ion.

$k = AT^n \exp(-E/RT)$, cm^3, mol, s

			At 2,000 K				
			ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
Neutral Reactions							
1.	$H + O_2 + M$	$= HO_2 + M$			7.0E+17	-0.8	0.0
2.	$H + O_2$	$= OH + O$			1.2E+17	-0.9	69.1
3.	$H + OH + M$	$= H_2O + M$			2.2E+22	-2.0	0.0
4.	$HO_2 + H$	$= H_2 + O_2$			2.5E+13	0.0	2.9
5.	$HO_2 + H$	$= OH + OH$			1.5E+14	0.0	4.2
6.	$HO_2 + OH$	$= H_2O + O_2$			2.0E+13	0.0	0.0
7.	$O + H_2$	$= OH + H$			1.5E+07	2.0	31.6
8.	$OH + H_2$	$= H_2O + H$			1.0E+08	1.6	13.8
9.	$OH + OH$	$= H_2O + O$			1.5E+09	1.1	-1.4
10.	$H_2 + M$	$= H + H + M$			2.2E+14	0.0	402.0
11.	$HCO + C_2H_3$	$= C_3H_4 + O$	150.0	203.0	1.0E+12	0.0	129.0
12.	$HCO + C_2H_4$	$= C_3H_4 + OH$	138.0	134.0	5.9E+11	0.0	142.0
13.	$HCO + M$	$= CO + H + M$			2.5E+14	0.0	70.3
14.	$CO + OH$	$= CO_2 + H$			4.4E+06	1.5	-3.1
15.	$CH + O$	$= CO + H$			4.0E+13	0.0	0.0
16.	$CH + O_2$	$= CO + OH$			2.0E+13	0.0	0.0
17.	$CH_2 + H$	$= CH + H_2$			4.0E+13	0.0	0.0
18.	$CH_2 + O$	$= CH + OH$			4.8E+10	0.0	0.0
19.	$CH_2 + O$	$= CO + H + H$			5.0E+13	0.0	0.0
20.	$CH_2 + O_2$	$= CO + H_2O$			3.9E+12	0.0	6.0
21.	$CH_2 + O_2$	$= CO + OH + H$			9.1E+12	0.0	6.0
22.	$CH_2CO + H$	$= CHCO + H_2$			3.0E+13	0.0	36.0
23.	$CH_2CO + M$	$= CO + CH_2 + M$			3.6E+15	0.0	248.0

TABLE III (Continued)

				At 2,000 K				
				ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
24.	$CH_2CO + O$	=	$HCO + HCO$			1.0E+13	0.0	25.0
25.	$CH_2CO + OH$	=	$CHCO + H_2O$			1.0E+13	0.0	11.0
26.	$CH_2O + C_2H_2$	=	$H_4C_3 + O$	386.0	10.6	1.1E+12	0.0	342.0
27.	$CH_2O + C_2H_3$	=	$C_3H_4 + OH$	93.8	93.0	8.5E+11	0.0	76.4
28.	$CH_2O + H$	=	$HCO + H_2$			2.5E+13	0.0	16.7
29.	$CH_2O + M$	=	$HCO + H + M$			3.7E+17	0.0	364.0
30.	$CH_2O + O$	=	$HCO + OH$			3.5E+13	0.0	14.7
31.	$CH_2O + OH$	=	$HCO + H_2O$			3.0E+13	0.0	5.0
32.	$CHCO + H$	=	$CH_2 + CO$			2.5E+13	0.0	0.0
33.	$CHCO + O$	=	$HCO + CO$			1.2E+12	0.0	0.0
34.	$C_2H + C_2H_3$	=	C_4H_4			1.0E+13	0.0	0.0
35.	$C_2H + H_2$	=	$H + C_2H_2$			8.0E+12	0.0	11.0
36.	$C_2H + O$	=	$CO + CH$			1.0E+13	0.0	0.0
37.	$C_2H + O_2$	=	$CHCO + O$			6.0E+11	0.0	0.0
38.	$C_2H + O_2$	=	$HCO + CO$			2.4E+12	0.0	0.0
39.	$C_2H + OH$	=	$C_2 + H_2O$			5.0E+13	0.0	25.0
40.	$C_2H_2 + C_2H$	=	$C_4H_2 + H$			3.5E+13	0.0	0.0
41.	$C_2H_2 + C_2H_2$	=	C_4H_4			1.3E+15	0.0	345.2
42.	$C_2H_2 + CH$	=	C_3H_3	-481.0	-219.0	3.0E+13	0.0	0.0
43.	$C_2H_2 + CH_2$	=	$C_3H_3 + H$	-41.8	-24.3	1.8E+12	0.0	14.7
44.	$C_2H_2 + M$	=	$C_2H + H + M$			4.2E+16	0.0	447.0
45.	$C_2H_2 + O$	=	$CH_2 + CO$			4.1E+08	1.5	7.1
46.	$C_2H_2 + O$	=	$CHCO + H$			4.3E+14	0.0	50.7
47.	$C_2H_2 + OH$	=	$C_2H + H_2O$			2.7E+14	0.0	63.0
48.	$C_2H_2 + OH$	=	$CH_2CO + H$			5.0E+14	0.0	60.0
49.	$C_2H_3 + C_4H_2$	=	$C_4H_4 + C_2H$			3.0E+13	0.0	96.0
50.	$C_2H_3 + H$	=	$C_2H_2 + H_2$			1.0E+13	0.0	0.0
51.	$C_2H_3 + H$	=	C_2H_4			7.1E+12	0.0	0.0
52.	$C_2H_3 + M$	=	$C_2H_2 + H + M$			1.2E+39	-7.2	213.0
53.	$C_2H_3 + O_2$	=	$CH_2O + HCO$			4.0E+12	0.0	-1.0
54.	$C_2H_4 + H$	=	$C_2H_3 + H_2$			6.9E+14	0.0	61.0
55.	$C_3H_2 + H$	=	C_3H_3	-336.0	-100.0	6.0E+12	0.0	0.0
56.	$C_3H_2 + O$	=	$C_2H + HCO$	-196.0	-224.0	6.8E+13	0.0	0.0
57.	$C_3H_2 + OH$	=	$C_2H_2 + HCO$	-277.0	109.0	6.8E+13	0.0	0.0
58.	$C_3H_3 + H$	=	H_4C_3	-389.0	-109.0	2.0E+13	0.0	0.0
59.	$C_3H_3 + O$	=	$C_3H_2 + OH$	-110.0	-119.0	3.2E+12	0.0	0.0
60.	$C_3H_3 + O_2$	=	$CH_2CO + HCO$	-360.0	-359.0	3.0E+10	0.0	12.0

TABLE III (Continued)

			At 2,000 K				
			ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
61.	$C_3H_4 + H$	= C_3H_5	-281.0	-55.8	1.2E+13	0.0	8.8
62.	$C_3H_4 + OH$	= $C_3H_3 + H_2O$	-134.0	-158.0	2.7E+11	0.0	0.0
63.	$C_4H_2 + O$	= $C_3H_2 + CO$	-368.0	-377.0	2.7E+13	0.0	7.2
64.	$C_4H_3 + H + M$	= $C_4H_4 + M$			1.0E+15	0.0	0.0
65.	$C_4H_3 + H$	= $C_4H_2 + H_2$			2.0E+13	0.0	0.0
66.	$C_4H_3 + M$	= $C_2H_2 + C_2H + M$			5.8E+10	0.0	220.0
67.	$C_4H_3 + M$	= $C_4H_2 + H + M$			1.0E+16	0.0	250.0
68.	$H_4C_3 + H$	= $CH_3 + C_2H_2$	-97.0	238.0	2.0E+13	0.0	10.0
69.	$H_4C_3 + H_2$	= $C_3H_5 + H$	181.0	173.0	1.0E+13	0.0	167.0
70.	$H_4C_3 + OH$	= $C_3H_3 + H_2O$	-127.0	-143.0	5.0E+12	0.0	5.4
71.	$H_4C_3 + M$	= $C_3H_4 + M$	7.87	15.6	7.8E+11	0.0	230.0
	Chemiionization/Excited State Reactions						
72.	$C_2 + OH$	→ $HC + CO$	-120.0	-94.0	3.4E+12	0.0	0.0
73.	$C_2H + O$	→ $HC + CO$	-71.0	-46.0	7.1E+11	0.0	0.0
74.	$C_2H + O_2$	→ $HC + CO_2$	-93.0	-35.0	4.5E+15	0.0	105.0
75.	$HC + M$	→ $CH + M$			4.0E+10	0.5	0.0
76.	$HC + O_2$	→ $CH + O_2$			2.4E+12	0.5	0.0
77.	HC	→ CH			1.7E+06	0.0	0.0
78.	$CH + O$	→ $HCO^+ + e$	18.0	201.0	1.4E+10	0.0	1.6
79.	$HC + O$	→ $HCO^+ + e$	-258.0	-80.0	4.8E+14	0.0	0.0
	Ion-Molecule Reaction						
80.	$HCO^+ + C_2H_2$	= $C_2H_3^+ + CO$	-60.0	-77.0	8.4E+14	0.0	0.0
81.	$C_3H_3^+ + OH$	= $HCO^+ + C_2H_3$	-119.0	-94.0	7.6E+14	-0.1	125.0
82.	$HCO^+ + C_3H_2$	= $C_3H3^+ + CO$	-288.0	-298.0	7.3E+14	0.0	0.0
83.	$HCO^+ + C_4H_2$	= $C_4H_3^+ + CO$	-176.0	-192.0	6.0E+14	0.0	0.0
84.	$HCO^+ + CH_2$	= $CH_3^+ + CO$	-245.0	-197.0	7.1E+14	0.0	0.0
85.	$HCO^+ + H_2O$	= $H_3O^+ + CO$	-127.0	-105.0	1.9E+15	0.0	0.0
86.	$HCO^+ + H_4C_3$	= $C_3H_3^+ + H_2 + CO$	54.2	-227.0	7.0E+14	0.0	0.0
87.	$H_3O^+ + C_3H_2$	= $C_3H_3^+ + H_2O$	-160.0	-193.0	8.6E+14	0.0	0.0
88.	$CH_3^+ + C_2H_2$	= $C_3H_3^+ + H_2$	-129.0	-151.0	6.0E+14	0.0	0.0

TABLE III (Continued)

		At 2,000 K				
		ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
89.	$CH_3^+ + C_4H_2 = C_3H_3^+ + C_2H_2$	-120.0	-160.0	7.0E+14	0.0	0.0
90.	$CH_3^+ + C_4H_2 = C_5H_3^+ + H_2$	-200.0	-245.0	7.8E+13	0.0	0.0
91.	$C_2H_3^+ + C_2H_2 = C_4H_3^+ + H_2$	-125.0	-106.0	3.0E+14	0.0	0.0
92.	$C_3H_3^+ + C_2H_2 = C_5H_3^+ + H_2$	-79.0	-85.0	3.0E+14	0.0	0.0
93.	$C_3H_3^+ + C_4H_2 = C_5H_3^+ + C_2H_2$	-71.0	-94.0	8.4E+14	0.0	0.0
94.	$C_3H_3^+ + C_4H_2 = C_7H_5^+$	-223.0	44.0	6.0E+14	0.0	0.0
95.	$C_3H_3^+ + H_4C_3 = C_4H_3^+ + C_2H_4$	-101.0	-79.0	6.6E+14	0.0	0.0
96.	$C_3H_3^+ + H_4C_3 = C_4H_5^+ + C_2H_2$	-135.0	-118.0	7.5E+14	0.0	0.0
97.	$C_3H_3^+ + H_4C_3 = C_6H_5^+ + H_2$	-174.0	-155.0	6.6E+14	0.0	0.0
98.	$C_3H_3^+ + M = H_3C_3^+ + M$	-107.0	-59.0	3.2E+15	0.0	0.0
99.	$C_7H_5^+ + H_2 = C_4H_3^+ + H_4C_3$	-7.21	-9.4	6.0E+14	0.0	0.0
100.	$C_4H_5^+ + C_2H_2 = C_6H_5^+ + H_2$	-40.0	-37.0	6.0E+14	0.0	0.0
101.	$C_4H_5^+ + C_4H_2 = C_8H_7^+$	-440.0	-36.0	6.0E+14	0.0	0.0
102.	$C_5H_3^+ + H_4C_3 = C_6H_5^+ + C_2H_2$	-95.0	-70.0	6.6E+14	0.0	0.0
103.	$C_6H_5^+ + H_4C_3 = C_7H_7^+ + C_2H_2$	-238.0	-111.0	6.5E+14	0.0	0.0
104.	$C_7H_5^+ + C_3H_4 = C_8H_7^+ + C_2H_2$	-360.0	-213.0	6.0E+14	0.0	0.0
105.	$C_9H_7^+ + H_2 = C_7H_7^+ + C_2H_2$	-31.0	-71.0	6.0E+13	0.0	0.0
106.	$C_8H_7^+ + C_2H_2 = C_{10}H_9^+$	-347.0	-6.6	6.0E+14	0.0	0.0
107.	$H_9C_{10}^+ = C_8H_7^+ + C_2H_2$	168.0	-117.0	6.0E+14	0.0	0.0
108.	$C_{11}H_9^+ + H_2 = C_8H_7^+ + H_4C_3$	94.0	-26.0	6.0E+14	0.0	0.0
109.	$C_{11}H_9^+ = C_9H_7^+ + C_2H_2$	296.0	-75.0	6.0E+14	0.0	0.0
110.	$H_9C_{11}^+ = C_9H_7^+ + C_2H_2$	225.0	-47.0	6.0E+14	0.0	0.0
111.	$C_9H_7^+ + H_4C_3 = C_{10}H_9^+ + C_2H_2$	-226.0	-163.0	6.0E+14	0.0	0.0
112.	$C_9H_7^+ + H_4C_3 = H_9C_{10}^+ + C_2H_2$	-46.0	-40.0	6.0E+14	0.0	0.0
113.	$C_{10}H_9^+ + C_2H_2 = C_{12}H_9^+ + H_2$	-170.0	-2.2	6.0E+14	0.0	0.0
114.	$H_9C_{12}^+ + H_2 = C_{10}H_9^+ + C_2H_2$	-68.0	-127.0	6.0E+14	0.0	0.0
115.	$H_9C_{10}^+ + C_2H_2 = C_{12}H_9^+ + H_2$	-349.0	-125.0	6.0E+14	0.0	0.0
116.	$H_9C_{12}^+ + H_2 = H_9C_{10}^+ + C_2H_2$	112.0	-4.0	6.0E+14	0.0	0.0
117.	$C_{10}H_9^+ + C_4H_2 = C_{12}H_9^+ + C_2H_2$	-161.0	-11.0	6.0E+14	0.0	0.0
118.	$H_9C_{12}^+ + C_2H_2 = C_{10}H_9^+ + C_4H_2$	-76.0	-118.0	6.0E+14	0.0	0.0
119.	$H_9C_{10}^+ + C_4H_2 = C_{12}H_9^+ + C_2H_2$	-341.0	-134.0	6.0E+14	0.0	0.0
120.	$H_9C_{10}^+ + C_4H_2 = H_9C_{12}^+ + C_2H_2$	-104.0	-409.0	6.0E+14	0.0	0.0
121.	$C_{13}H_9^+ + H_2 = C_{11}H_9^+ + C_2H_2$	257.0	-91.0	6.0E+14	0.0	0.0
122.	$C_{13}H_9^+ + H_2 = H_9C_{11}^+ + C_2H_2$	328.0	-119.0	6.0E+14	0.0	0.0
123.	$C_{13}H_9^+ + C_2H_2 = C_{11}H_9^+ + C_4H_2$	249.0	-82.0	6.0E+14	0.0	0.0

TABLE III (Continued)

		At 2,000 K				
		ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
124.	$C_{13}H_9^+ + C_2H_2 = H_9C_{11}^+ + C_4H_2$	320.0	-110.0	6.0E+14	0.0	0.0
125.	$C_{14}H_{11}^+ + H_2 = C_{11}H_9^+ + H_4C_3$	207.0	-105.0	6.0E+14	0.0	0.0
126.	$C_{14}H_{11}^+ + H_2 = H_9C_{11}^+ + H_4C_3$	279.0	-133.0	6.0E+14	0.0	0.0
127.	$C_{14}H_{11}^+ = C_{12}H_9^+ + C_2H_2$	109.0	-345.0	6.0E+14	0.0	0.0
128.	$C_{14}H_{11}^+ = H_9C_{12}^+ + C_2H_2$	346.0	-216.0	6.0E+14	0.0	0.0
129.	$C_{15}H_{11}^+ + H_2 = C_{12}H_9^+ + H_4C_3$	-87.3	-118.4	6.0E+14	0.0	0.0
130.	$H_9C_{12}^+ + H_4C_3 = C_{15}H_{11}^+ + H_2$	-149.0	-11.0	6.0E+14	0.0	0.0
131.	$C_{13}H_9^+ + C_2H_2 = C_{15}H_{11}^+$	-78.0	-6.8	6.0E+14	0.0	0.0
132.	$C_{14}H_{11}^+ + C_2H_2 = C_{13}H_9^+ + H_4C_3$	-49.0	-14.0	1.4E+14	0.0	0.0
133.	$C_{13}H_9^+ + H_4C_3 = C_{16}H_{11}^+ + H_2$	-312.0	-547.0	6.0E+14	0.0	0.0
134.	$C_{14}H_{11}^+ + C_2H_2 = C_{16}H_{11}^+ + H_2$	-362.0	-561.0	6.0E+14	0.0	0.0
135.	$C_{14}H_{11}^+ + C_4H_2 = C_{16}H_{11}^+ + C_2H_2$	-354.0	-570.0	6.0E+14	0.0	0.0
136.	$C_{15}H_{11}^+ + C_2H_2 = C_{17}H_{11}^+ + H_2$	-260.0	-167.0	6.0E+14	0.0	0.0
137.	$C_{15}H_{11}^+ + C_2H_2 = H_{11}C_{17}^+ + H_2$	-418.0	-290.0	6.0E+14	0.0	0.0
138.	$C_{15}H_{11}^+ + C_4H_2 = C_{17}H_{11}^+ + C_2H_2$	-252.0	-176.0	6.0E+14	0.0	0.0
139.	$C_{15}H_{11}^+ + C_4H_2 = H_{11}C_{17}^+ + C_2H_2$	-410.0	-299.0	6.0E+14	0.0	0.0
140.	$C_{18}H_{11}H^+ + H_2 = C_{16}H_{11}^+ + C_2H_2$	-123.0	-317.0	6.0E+14	0.0	0.0
141.	$H_{11}C_{18}^+ + H_2 = C_{16}H_{11}^+ + C_2H_2$	-21.0	-126.0	6.0E+14	0.0	0.0
142.	$C_{18}H_{11}H^+ + C_2H_2 = C_{16}H_{11}^+ + C_4H_2$	-131.0	-308.0	6.0E+14	0.0	0.0
143.	$H_{11}C_{18}^+ + C_2H_2 = C_{16}H_{11}^+ + C_4H_2$	-29.0	-117.0	6.0E+14	0.0	0.0
144.	$H_{11}C_{20}^+ + H_2 = C_{16}H_{11}^+ + C_4H_2$	247.0	-7.4	6.0E+14	0.0	0.0
145.	$C_{17}H_{11}^+ + C_2H_2 = C_{19}H_{11}^+ + H_2$	-374.0	-215.0	6.0E+14	0.0	0.0
146.	$H_{11}C_{17}^+ + C_2H_2 = C_{19}H_{11}^+ + H_2$	-216.0	-92.0	6.0E+14	0.0	0.0
147.	$C_{17}H_{11}^+ + C_4H_2 = C_{21}H_{11}^+ + H_2$	-441.0	-270.0	6.0E+14	0.0	0.0
148.	$C_{17}H_{11}^+ + C_4H_2 = C_{19}H_{11}^+ + C_2H_2$	-365.0	-224.0	6.0E+14	0.0	0.0
149.	$H_{11}C_{17}^+ + C_4H_2 = C_{19}H_{11}^+ + C_2H_2$	-208.0	-101.0	6.0E+14	0.0	0.0
150.	$C_{18}H_{11}^+ + C_2H_2 = H_{11}C_{20}^+ + H_2$	-378.0	-300.0	6.0E+14	0.0	0.0
151.	$H_{11}C_{18}^+ + C_2H_2 = H_{11}C_{20}^+ + H_2$	-276.0	-109.0	6.0E+14	0.0	0.0
152.	$C_{18}H_{11}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	-370.0	-309.0	6.0E+14	0.0	0.0
153.	$H_{11}C_{18}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	-277.0	-118.0	6.0E+14	0.0	0.0
154.	$C_{19}H_{11}^+ + C_2H_2 = C_{21}H_{11}^+ + H_2$	-76.0	-46.0	6.0E+14	0.0	0.0
155.	$C_{19}H_{11}^+ + C_4H_2 = C_{21}H_{11}^+ + C_2H_2$	-68.0	-55.0	6.0E+14	0.0	0.0
156.	$C_{19}H_{11}^+ + H_4C_3 = C_{22}H_{13}^+ + H_2$	-198.0	-268.0	6.0E+14	0.0	0.0
157.	$C_{20}H_{11}^+ + C_2H_2 = C_{22}H_{13}^+$	-492.0	-311.0	6.0E+14	0.0	0.0
158.	$H_{11}C_{20}^+ + C_2H_2 = C_{22}H_{13}^+$	-342.0	-126.0	6.0E+14	0.0	0.0
159.	$C_{20}H_{11}^+ + H_4C_3 = C_{23}H_{13}^+ + H_2$	-332.0	-233.0	6.0E+14	0.0	0.0

TABLE III (Continued)

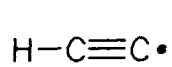
		At 2,000 K				
		ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
160.	$H_{11}C_{20}^+ + H_4C_3 = C_{23}H_{13}^+ + H_2$	-182.0	-48.0	6.0E+14	0.0	0.0
161.	$C_{23}H_{13}^+ = C_{21}H_{11}^+ + C_2H_2$	285.0	-62.0	6.0E+14	0.0	0.0
162.	$C_{21}H_{11}^+ + H_4C_3 = C_{24}H_{13}^+ + H_2$	-306.0	-285.0	6.0E+14	0.0	0.0
163.	$C_{21}H_{11}^+ + H_4C_3 = C_{22}H_{13}^+ + C_2H_2$	-122.0	-222.0	6.0E+14	0.0	0.0
164.	$C_{22}H_{13}^+ + C_2H_2 = C_{24}H_{13}^+ + H_2$	-184.0	-62.0	6.0E+14	0.0	0.0
165.	$C_{22}H_{13}^+ + C_4H_2 = C_{24}H_{13}^+ + C_2H_2$	-175.0	-71.0	6.0E+14	0.0	0.0
	Ion-Electron Recombination Reactions					
166.	$H_3O^+ + e \rightarrow H_2O + H$	-627.0	-768.0	1.2E+17	0.0	0.0
167.	$HCO^+ + e \rightarrow CO + H$	-754.0	-873.0	1.2E+17	0.0	0.0
168.	$CH_3^+ + e \rightarrow CH + H_2$	-523.0	-678.0	1.2E+17	0.0	0.0
169.	$C_2H_3^+ + e \rightarrow C_2H + H_2$	-581.0	-731.0	1.2E+17	0.0	0.0
170.	$C_3H_3^+ + e \rightarrow C_2H_2 + CH$	-395.0	-545.0	1.2E+17	0.0	0.0
171.	$H_3C_3^+ + e \rightarrow C_2H_2 + CH$	-287.0	-486.0	1.2E+17	0.0	0.0
172.	$C_4H_3^+ + e \rightarrow C_2H_2 + C_2H$	-456.0	-625.0	1.2E+17	0.0	0.0
173.	$C_4H_5^+ + e \rightarrow C_2H_2 + C_2H_3$	-592.0	-631.0	1.2E+17	0.0	0.0
174.	$C_5H_3^+ + e \rightarrow C_3H_3 + C_2$	-188.0	-346.0	1.2E+17	0.0	0.0
175.	$C_5H_3^+ + e \rightarrow C_2H + C_3H_2$	-274.0	-426.0	1.2E+17	0.0	0.0
176.	$C_7H_5^+ + e \rightarrow C_4H_2 + C_3H_3$	-653.0	-808.0	1.2E+17	0.0	0.0
177.	$C_6H_5^+ + e \rightarrow C_4H_4 + C_2H$	-440.0	-592.0	1.2E+17	0.0	0.0
178.	$C_7H_5^+ + e \rightarrow C_5H_5 + C_2$			1.2E+17	0.0	0.0
179.	$C_7H_7^+ + e \rightarrow C_6H_4 + CH_3$			1.2E+17	0.0	0.0
180.	$C_7H_7^+ + e \rightarrow C_6H_6 + CH$	-258.0	-383.0	1.2E+17	0.0	0.0
181.	$C_8H_7^+ + e \rightarrow C_6H_6 + C_2H$	-573.0	-548.0	1.2E+17	0.0	0.0
182.	$C_9H_7^+ + e \rightarrow C_8H_6 + CH$			1.2E+17	0.0	0.0
183.	$C_{10}H_9^+ + e \rightarrow C_{10}H_8 + H$	-529.0	-578.0	1.2E+17	0.0	0.0
184.	$H_9C_{10}^+ + e \rightarrow C_8H_6 + C_2H_3$			1.2E+17	0.0	0.0
185.	$C_{11}H_9^+ + e \rightarrow C_{10}H_8 + CH$	-368.0	-508.0	1.2E+17	0.0	0.0
186.	$H_9C_{11}^+ + e \rightarrow C_8H_6 + C_3H_3$			1.2E+17	0.0	0.0
187.	$C_{12}H_9^+ + e \rightarrow C_{12}H_8 + H$			1.2E+17	0.0	0.0
188.	$H_9C_{12}^+ + e \rightarrow C_{10}H_8 + C_2H$	-482.0	-640.0	1.2E+17	0.0	0.0
189.	$C_{13}H_9^+ + e \rightarrow C_{13}H_9$			1.2E+17	0.0	0.0
190.	$C_{13}H_9^+ + e \rightarrow C_{12}H_8 + CH$			1.2E+17	0.0	0.0

TABLE III (Continued)

		At 2,000 K				
		ΔH_f, kJ	ΔG_f, kJ	A	n	E, kJ
191.	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{10} + H$			1.2E+17	0.0	0.0
192.	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{11}$			1.2E+17	0.0	0.0
193.	$C_{15}H_{11}^+ + e \rightarrow C_{14}H_{10} + CH$			1.2E+17	0.0	0.0
194.	$C_{15}H_{11}^+ + e \rightarrow C_{15}H_{11}$			1.2E+17	0.0	0.0
195.	$C_{16}H_{11}^+ + e \rightarrow C_{16}H_{10} + H$			1.2E+17	0.0	0.0
196.	$C_{17}H_{11}^+ + e \rightarrow C_{17}H_{10} + H$			1.2E+17	0.0	0.0
197.	$C_{17}H_{11}^+ + e \rightarrow C_{16}H_{10} + CH$			1.2E+17	0.0	0.0
198.	$H_{11}C_{17}^+ + e \rightarrow C_{17}H_{11}$			1.2E+17	0.0	0.0
199.	$H_{11}C_{18}^+ + e \rightarrow C_{16}H_{10} + C_2H$			1.2E+17	0.0	0.0
200.	$C_{18}H_{10}H^+ + e \rightarrow C_{18}H_{10} + H$			1.2E+17	0.0	0.0
201.	$C_{19}H_{11}^+ + e \rightarrow C_{19}H_{11}$			1.2E+17	0.0	0.0
202.	$C_{19}H_{11}^+ + e \rightarrow C_{18}H_{10} + CH$			1.2E+17	0.0	0.0
203.	$C_{20}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_2H$			1.2E+17	0.0	0.0
204.	$H_{11}C_{20}^+ + e \rightarrow C_{20}H_{11}$			1.2E+17	0.0	0.0
205.	$C_{21}H_{11}^+ + e \rightarrow C_{21}H_{11}$			1.2E+17	0.0	0.0
206.	$C_{21}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_3H$			1.2E+17	0.0	0.0
207.	$C_{22}H_{13}^+ + e \rightarrow C_{22}H_{12} + H$			1.2E+17	0.0	0.0
208.	$C_{23}H_{13}^+ + e \rightarrow C_{22}H_{12} + CH$			1.2E+17	0.0	0.0
209.	$C_{23}H_{13}^+ + e \rightarrow C_{23}H_{13}$			1.2E+17	0.0	0.0
210.	$C_{24}H_{13}^+ + e \rightarrow C_{24}H_{12} + H$			1.2E+17	0.0	0.0

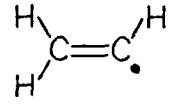
These factors have been applied to Reactions: 1, 3, 10, 13, 23 and 29:

H_2	Enhanced by 1.000E+00
O_2	Enhanced by 4.000E-01
C_2H_2	Enhanced by 1.000E+00
CO	Enhanced by 7.500E-01
CO_2	Enhanced by 1.500E+00
H_2O	Enhanced by 6.500E+00
Ar	Enhanced by 3.500E-01



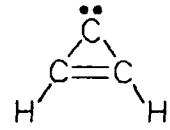
C_2H

(C_2H)



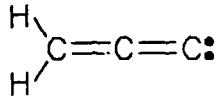
C_2H_3

(C_2H_3)



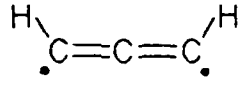
C_3H_2 (a)

(HC_3H)



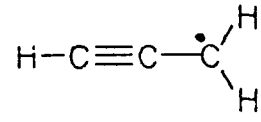
C_3H_2(b)

(H_2C_3)



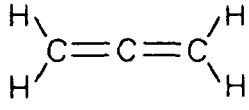
C_3H_2(c)

(C_3H_2)



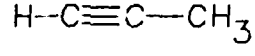
C_3H_3

(C_3H_3)



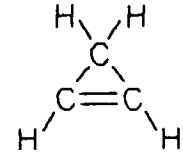
C_3H_4(a)

(C_3H_4)



C_3H_4(b)

(H_4C_3)

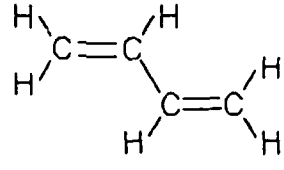


C_3H_4(c)

($H_2C_3H_2$)

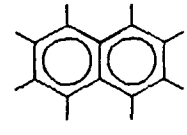
C_4H_2

(C_4H_2)



C_4H_6

(C_4H_6)

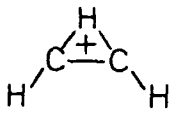


$C_{10}H_8$

($C_{10}H_8$)

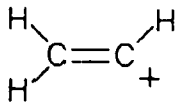
FIGURE 1 MOLECULAR STRUCTURES FOR NEUTRAL AND RADICAL SPECIES

The upper formula is the standard notation;
the lower formula is used in the kinetics reaction
mechanism to accommodate the computer program requirements.



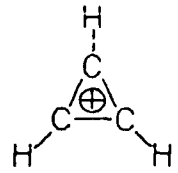
$C_2H_3^+$ (a)

$(C_2H_3^+)$



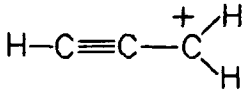
$C_2H_3^+$ (b)

$(H_3C_2^+)$



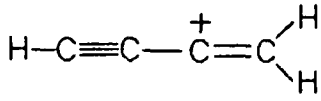
$C_3H_3^+$ (a)

$(H_3C_3^+)$



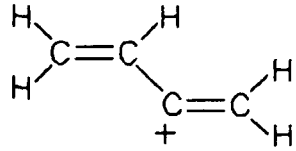
$C_3H_3^+$(b)

$(C_3H_3^+)$



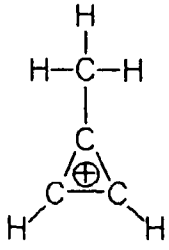
$C_4H_3^+$

$(C_4H_3^+)$



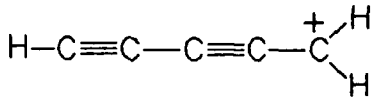
$C_4H_5^+$ (a)

$(C_4H_5^+)$



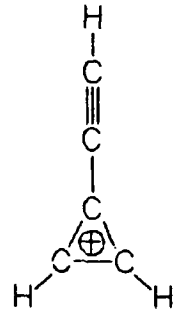
$C_4H_5^+$(b)

$(H_5C_4^+)$



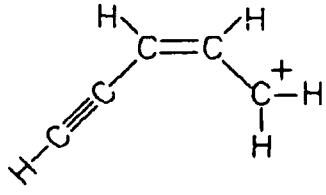
$C_5H_3^+$(a)

$(C_5H_3^+)$



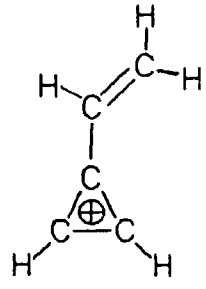
$C_5H_3^+$(b)

$(H_3C_5^+)$



$C_5H_5^+$(a)

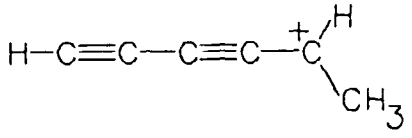
$(C_5H_5^+)$



$C_5H_5^+$(b)

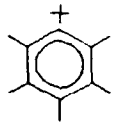
$(H_5C_5^+)$

FIGURE 2 MOLECULAR STRUCTURES FOR CATIONS



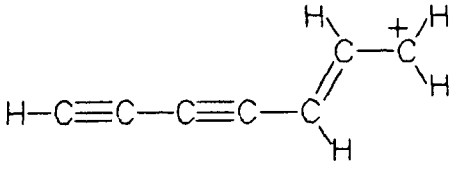
$C_6H_5^+$ (a)

$(C_6H_5^+)$



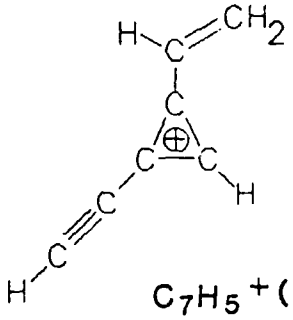
$C_6H_5^+$(b)

$(H_5C_6^+)$



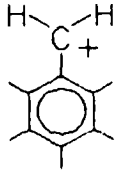
$C_7H_5^+$(a)

$(C_7H_5^+)$



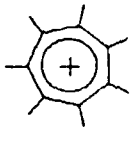
$C_7H_5^+$(b)

$(H_5C_7^+)$



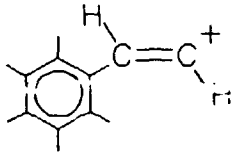
$C_7H_7^+$(a)

$(C_7H_7^+)$



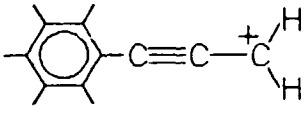
$C_7H_7^+$(b)

$(H_7C_7^+)$



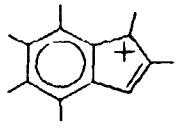
$C_8H_7^+$

$(C_8H_7^+)$



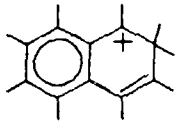
$C_9H_7^+$(a)

$(C_9H_7^+)$



$C_9H_7^+$(b)

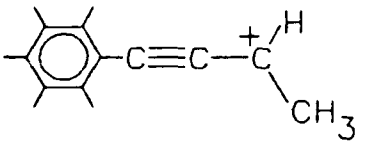
$(H_7C_9^+)$



$C_{10}H_9^+$(a)

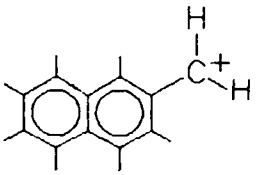
$(C_{10}H_9^+)$

FIGURE 2 (Continued)



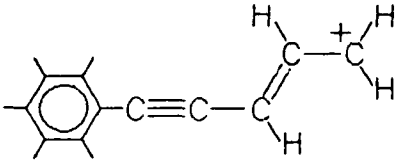
$C_{10}H_9^+$ (b)

$(H_9C_{10}^+)$



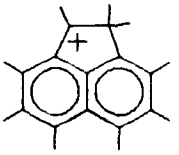
$C_{11}H_9^+$ (a)

$(C_{11}H_9^+)$



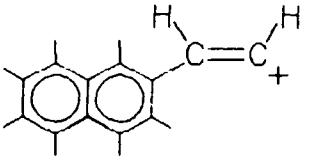
$C_{11}H_9^+$ (b)

$(H_9C_{11}^+)$



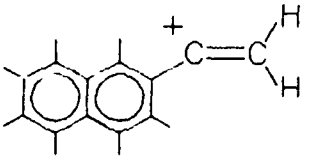
$C_{12}H_9^+$ (a)

$(C_{12}H_9^+)$



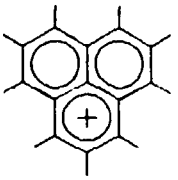
$C_{12}H_9^+$ (b)

$(H_9C_{12}^+)$



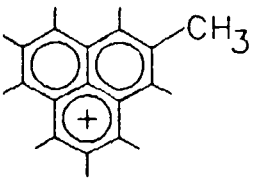
$C_{12}H_9^+$ (c)

$(C_{12}H_8H^+)$



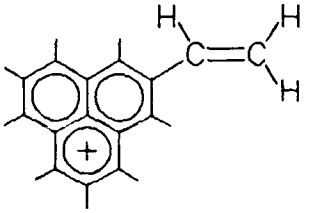
$C_{13}H_9^+$

$(C_{13}H_9^+)$



$C_{14}H_{11}^+$

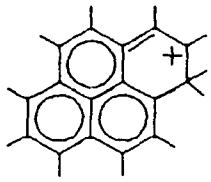
$(C_{14}H_{11}^+)$



$C_{15}H_{11}^+$

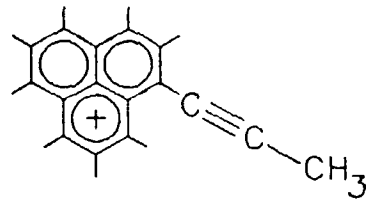
$(C_{15}H_{11}^+)$

FIGURE 2 (Continued)



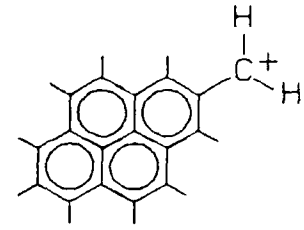
$C_{16}H_{11}^{+}$(a)

($C_{16}H_{11}^{+}$)



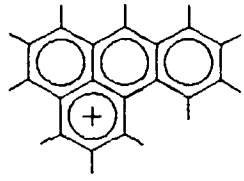
$C_{16}H_{11}^{+}$(b)

($H_{11}C_{16}^{+}$)



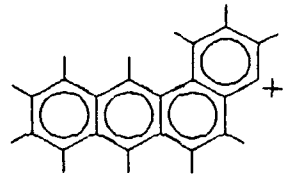
$C_{17}H_{11}^{+}$(a)

($C_{17}H_{11}^{+}$)



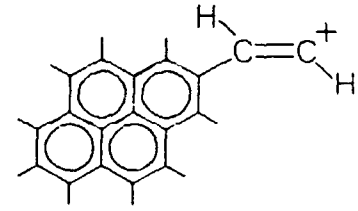
$C_{17}H_{11}^{+}$(b)

($H_{11}C_{17}^{+}$)



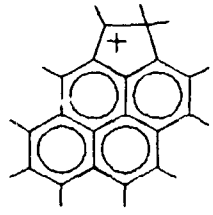
$C_{18}H_{11}^{+}$(a)

($C_{18}H_{11}^{+}$)



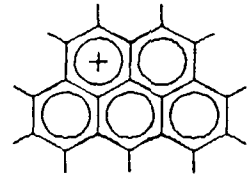
$C_{18}H_{11}^{+}$ (b)

($H_{11}C_{18}^{+}$)



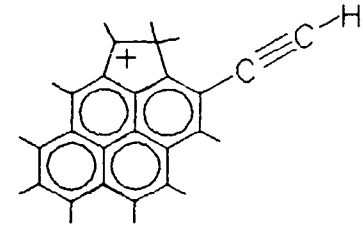
$C_{18}H_{11}^{+}$(c)

($C_{18}H_{10}H^{+}$)



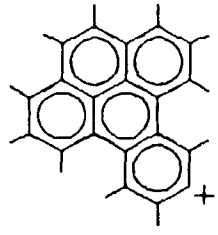
$C_{19}H_{11}^{+}$

($C_{19}H_{11}^{+}$)



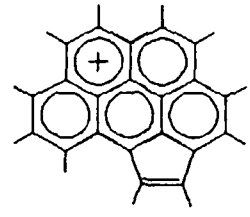
$C_{20}H_{11}^{+}$ (a)

($C_{20}H_{11}^{+}$)



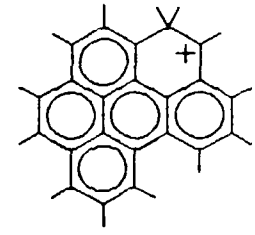
$C_{20}H_{11}^{+}$(b)

($H_{11}C_{20}^{+}$)



$C_{21}H_{11}^{+}$

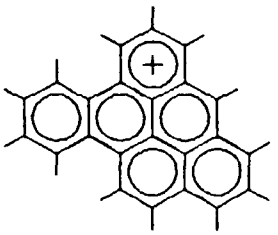
($C_{21}H_{11}^{+}$)



$C_{22}H_{13}^{+}$

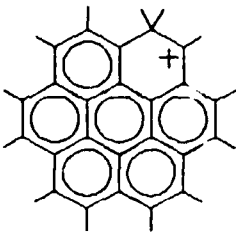
($C_{22}H_{13}^{+}$)

FIGURE 2 (Continued)



$C_{23}H_{13}^{+}$

$(C_{23}H_{13}^{+})$



$C_{24}H_{13}^{+}$

$(C_{24}H_{13}^{+})$

FIGURE 2 (Continued)

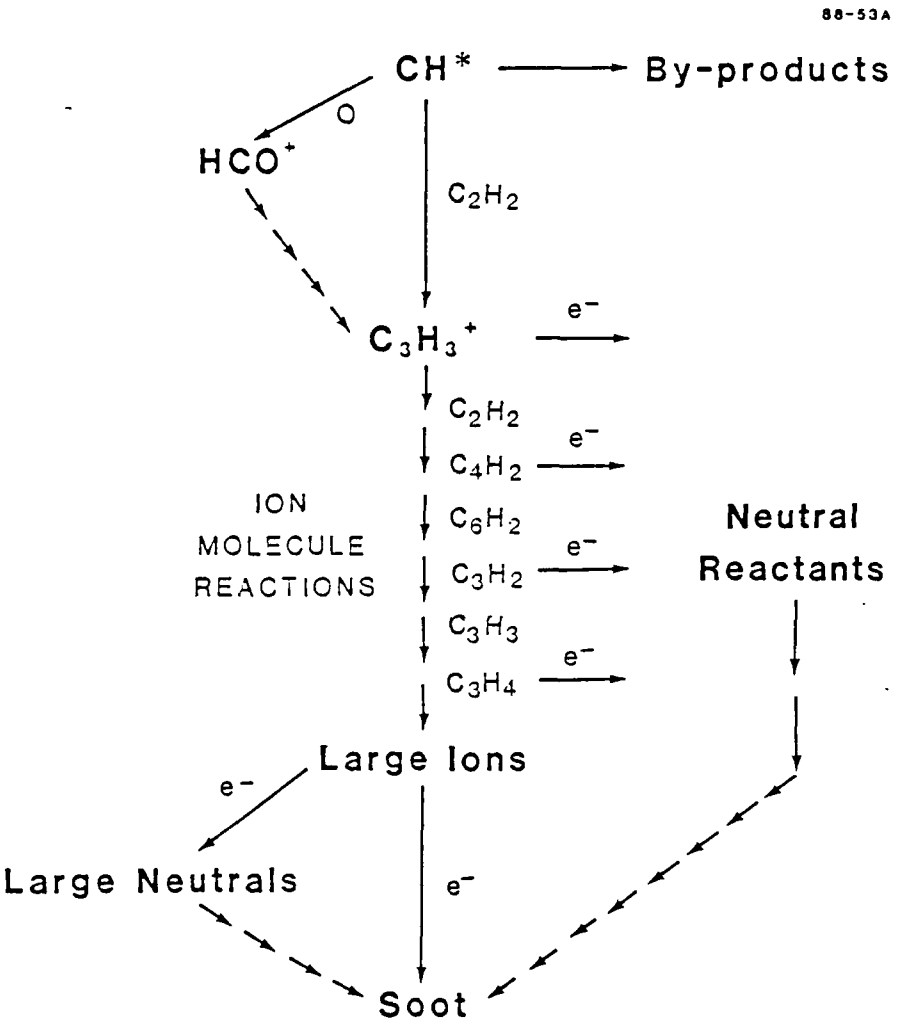


FIGURE 3 IONIC MECHANISM OF SOOT FORMATION